



Europäisches Patentamt  
European Patent Office  
Office européen des brevets



Publication number: **0 594 133 A2**

(12)

## EUROPEAN PATENT APPLICATION

(21) Application number: 93116889.2

(51) Int. Cl.<sup>5</sup>: C08G 59/68, C08G 59/66

(22) Date of filing: 19.10.93

(30) Priority: 22.10.92 JP 284300/92  
23.08.93 JP 227851/93  
23.08.93 JP 227852/93

(43) Date of publication of application:  
27.04.94 Bulletin 94/17

(84) Designated Contracting States:  
DE FR GB

(71) Applicant: AJINOMOTO CO., INC.  
15-1, Kyobashi 1-chome, Chuo-ku  
Tokyo 104(JP)

(72) Inventor: Sakata, Hiroyuki, c/o Central  
Research Lab.  
Ajinomoto Co., Inc.,  
1-1 Suzuki-cho,  
Kawasaki-ku  
Kawasaki-shi, Kanagawa-ken(JP)  
Inventor: Yokota, Tadahiko, c/o Central  
Research Lab.  
Ajinomoto Co., Inc.,  
1-1 Suzuki-cho,  
Kawasaki-ku  
Kawasaki-shi, Kanagawa-ken(JP)  
Inventor: Mori, Kenichi, c/o Central Research  
Lab.

Ajinomoto Co., Inc.,  
1-1 Suzuki-cho,  
Kawasaki-ku  
Kawasaki-shi, Kanagawa-ken(JP)  
Inventor: Hirai, Kiyomiki, c/o Central Research  
Lab.

Ajinomoto Co., Inc.,  
1-1 Suzuki-cho,  
Kawasaki-ku  
Kawasaki-shi, Kanagawa-ken(JP)  
Inventor: Takeuchi, Koji, c/o Central Research  
Lab.

Ajinomoto Co., Inc.,  
1-1 Suzuki-cho,  
Kawasaki-ku  
Kawasaki-shi, Kanagawa-ken(JP)  
Inventor: Hatajima, Toshihiko, c/o Central  
Research Lab.  
Ajinomoto Co., Inc.,  
1-1 Suzuki-cho,  
Kawasaki-ku  
Kawasaki-shi, Kanagawa-ken(JP)

(74) Representative: Strehl Schübel-Hopf Groening  
& Partner  
Maximilianstrasse 54  
D-80538 München (DE)

(54) Polythiol epoxy resin composition with extended working life.

(57) An epoxy resin composition which contains (1) an epoxy resin which has 2 or more epoxy groups in its molecule, (2) a polythiol compound which has 2 or more thiol groups in its molecule and (3) a solid dispersion-type amine adduct latent curing accelerator or the product of a reaction between a compound which contains one or more isocyanate groups in its molecule and a compound which has at least one primary and/or secondary amino group in its molecule.

EP 0 594 133 A2

Field of the Invention

The present invention relates to a polythiol epoxy resin composition which cures rapidly at relatively low heating temperatures, provides a strong adhesive strength and long working life and thus is suitable for processing.

Description of the Prior Art

Epoxy resin compositions which use polythiol as a curing agent and a liquid tertiary amine as an accelerator are known as low-temperature, rapid-curing epoxy resin compositions which can cure at -20 °C to 0 °C, and these are widely used in adhesives, sealing agents, casting materials and the like.

However, such epoxy resin compositions are disadvantageous in that their pot life is very short, usually a few seconds to a few minutes after mixing, and thus there is not enough time for mixing, defoaming and application. Also, since the user must prepare a new composition each time, the working efficiency is lowered, and since the excess composition cannot be preserved it must be disposed of, which is disadvantageous from the point of view of conservation of resources and environmental problems.

It has therefore been desired to develop a polythiol epoxy resin composition which has a sufficiently long working life and a good working efficiency. Nevertheless, the commercially available epoxy resins which contain thiol compounds generally have poor shelf life, and it is difficult to increase the working life of epoxy resin compositions when used with thiol curing agents.

As a method to solve such problems, a method is being investigated in which an acid anhydride or mercapto organic acid is added to the resin as a retarder to lengthen the working life thereof (Japanese laid-open patent application S61-159417), but this method cannot be said to be sufficiently satisfactory.

On the other hand, examples of a thiol compound obtained by a esterification reaction between a polythiol and an organic mercapto acid which is used as a curing agent for epoxy resins are described in Japanese laid-open patent application S41-7236, Japanese laid-open patent application S42-26535, Japanese laid-open patent application S47-32319, Japanese laid-open patent application S46-732 and Japanese laid-open patent application S60-21648, but the accelerators used in these epoxy resin compositions are liquid amines, etc. Also, the compositions using these liquid amines, etc. have a very short working life of from a few minutes to a few dozen minutes, which is a serious disadvantage for use.

Brief Summary of the Invention

The object of the present invention is to provide a polythiol epoxy resin composition which has a sufficiently long working life, cures rapidly at relatively low heating temperatures, and has a strong adhesive strength.

Detailed Description of the Invention

The inventors of the present invention, as a result of diligent research aimed at overcoming the above mentioned problems, have discovered that a polythiol epoxy resin composition which has a sufficiently long working life, cures rapidly at relatively low heating temperatures, and also has a strong adhesive strength may be obtained by using as the curing agent a polythiol compound which has 2 or more thiol groups in its molecule and using as the curing accelerator a solid dispersion-type amine adduct latent curing accelerator or the product of a reaction between a compound which contains one or more isocyanate groups in its molecule and a compound which has at least one primary and/or secondary amino group in its molecule, and thus the present invention has been completed.

The present invention relates to an epoxy resin composition which contains (1) an epoxy resin which has 2 or more epoxy groups in its molecule, (2) a polythiol compound which has 2 or more thiol groups in its molecule and (3) a solid dispersion-type amine adduct latent curing accelerator or a compound obtained as the product of a reaction between a compound which contains one or more isocyanate groups in its molecule and a compound which has at least one primary and/or secondary amino group in its molecule.

The epoxy resin to be used according to the present invention may be any one which has an average of 2 or more epoxy groups per molecule. Examples thereof include polyglycidyl ethers which are obtained by reacting a polyhydric phenol such as bisphenol A, bisphenol F, bisphenol AD, catechol, resorcinol, etc. or a polyhydric alcohol such as glycerol or polyethylene glycol, etc. with epichlorohydrin; glycidyl ether esters which are obtained by reacting a hydroxycarboxylic acid such as p-hydroxybenzoic acid or  $\beta$ -hydroxynaphthoic acid with epichlorohydrin; polyglycidyl esters which are obtained by reacting a polycar-

boxylic acid such as phthalic acid or terephthalic acid with epichlorohydrin; as well as epoxidized phenol novolac resins, epoxidized cresol novolac resins, epoxidized polyolefins, cyclicaliphatic epoxy resins, and also urethane modified epoxy resins and the like, but it is not limited to these examples.

The polythiol compound to be used according to the present invention is a thiol compound which has 2 or more thiol groups in its molecule, and which does not require the use of a basic substance for its production, such as a thiol compound obtained by the esterification reaction of an organic mercapto acid with a polythiol such as, for example, trimethylolpropane tris-(thioglycolate), pentaerythritol tetrakis-(thioglycolate), ethyleneglycol dithioglycolate, trimethylolpropane tris-( $\beta$ -thiopropionate)-pentaerythritoltetracys-( $\beta$ -thiopropionate), dipentaerythritol poly( $\beta$ -thiopropionate), etc.

In the same manner, thiol compounds with 2 or more thiol groups in their molecules may be used for which basic substances are used as reaction catalysts during the steps of their production, combined with dealkalizing treatment to reduce the alkali metal ion concentration to 50 ppm or less, including alkyl polythiol compounds such as 1,4-butanedithiol, 1,6-hexanedithiol and 1,10-decanedithiol; terminal thiol group-containing polyethers, terminal thiol group-containing polythioethers, thiol compounds obtained by the reaction of an epoxy compound with hydrogen sulfide; and thiol compounds containing a terminal thiol group which are obtained by a reaction of a polythiol compound with an epoxy compound.

As the method for dealkalization treatment of the polythiol compounds prepared using a basic substance as a reaction catalyst may be mentioned, for example, a method in which the thiol compound to be treated is dissolved in an organic solvent such as acetone or methanol, and an acid such as dilute hydrochloric acid or dilute sulfuric acid is added thereto for neutralization, after which extraction and washing are carried out for desalting, a method of adsorption using anion-exchange resin, a method of purification by distillation, etc., but it is not limited to these methods.

The solid dispersion-type amine adduct latent curing accelerator to be used according to the present invention is the product of the reaction between an amine compound and an epoxy compound which is a solid insoluble in the epoxy resin at room temperature and which functions as an accelerator by becoming soluble upon heating; this also includes those reaction products whose surfaces have been treated with an isocyanate compound or acidic compound, etc.

As examples of the epoxy compound to be used as a starting material for the production of the latent curing accelerator which is used according to the present invention may be mentioned polyfunctional epoxy compounds such as polyglycidyl ethers which are obtained by reacting a polyhydric phenol such as bisphenol A, bisphenol F, catechol, resorcinol, etc. or a polyhydric alcohol such as glycerol or polyethylene glycol, etc. with epichlorohydrin; glycidyl ether esters which are obtained by reacting a hydroxycarboxylic acid such as p-hydroxybenzoic acid or  $\beta$ -hydroxynaphthoic acid with epichlorohydrin; polyglycidyl esters which are obtained by reacting a polycarboxylic acid such as phthalic acid or terephthalic acid with epichlorohydrin; glycidylamine compounds which are obtained by reacting 4,4'-diaminodiphenylmethane, m-aminophenol or the like with epichlorohydrin; and epoxidized phenol novolac resins, epoxidized cresol novolac resins, epoxidized polyolefins, as well as monofunctional epoxy compounds such as butyl glycidyl ethers, phenyl glycidyl ethers, glycidyl methacrylate and the like, but the epoxy compound is not limited to these examples.

The amine compound to be used as a starting material for the production of the latent curing accelerator which is used according to the present invention may be any one which has in its molecule one or more active hydrogens capable of an addition reaction with an epoxy group, as well as one or more substituents selected from primary, secondary and tertiary amino groups. Examples of such an amine compound are given below, but it is not limited thereto.

It may be, for example, an aliphatic amine such as diethylenetriamine, triethylenetetraamine, n-propylamine, 2-hydroxyethylaminopropylamine, cyclohexylamine, 4,4'-diaminodicyclohexylmethane; an aromatic amine compound such as 4,4'-diaminodiphenylmethane, 2-methylaniline, etc.; or a nitrogen comprising heterocyclic compound such as 2-ethyl-4-methylimidazole, 2-methylimidazole, 2-ethyl-4-methylimidazoline, 2,4-dimethylimidazoline, piperidine, piperazine, etc.

Furthermore, of these compounds, particularly those which have tertiary amino groups in their molecules are materials which will provide latent curing accelerators with excellent accelerating properties, and examples of such compounds include, for example, amine compounds such as dimethylaminopropylamine, diethylaminopropylamine, di-n-propylaminopropylamine, dibutylaminopropylamine, dimethylaminoethylamine, diethylaminoethylamine, N-methylpiperazine, etc.; primary and secondary amines which have a tertiary amino group in their molecules, such as imidazole compounds like 2-methylimidazole, 2-ethylimidazole, 2-ethyl-4-methylimidazole, 2-phenylimidazole, etc.; and alcohols, phenols, thiols, carboxylic acids, hydrazides, etc. which have a tertiary amino group in their molecules, including 2-dimethylaminoethanol, 1-methyl-2-dimethylaminoethanol, 1-phenoxyethyl-2-



dimethylaminoethanol, 2-diethylaminoethanol, 1-butoxymethyl-2-dimethylaminoethanol, 1-(2-hydroxy-3-phenoxypropyl)-2-methylimidazole, 1-(2-hydroxy-3-phenoxypropyl)-2-ethyl-4-methylimidazole, 1-(2-hydroxy-3-butoxypropyl)-2-methylimidazole, 1-(2-hydroxy-3-butoxypropyl)-2-ethyl-4-methylimidazole, 1-(2-hydroxy-3-phenoxypropyl)-2-phenylimidazoline, 1-(2-hydroxy-3-butoxypropyl)-2-methylimidazoline, 2-(dimethylaminomethyl) phenol, 2,4,6-tris(dimethylaminomethyl) phenol, N- $\beta$ -hydroxyethylmorpholine, 2-dimethylaminoethanethiol, 2-mercaptopyridine, 2-mercaptobenzoimidazole, 2-mercaptobenzothiazole, 4-mercaptopyridine, N,N-dimethylaminobenzoic acid, N,N-dimethylglycine, nicotinic acid, isonicotinic acid, picolinic acid, N,N-dimethylglycine hydrazide, N,N-dimethylpropionic acid hydrazide, nicotinic acid hydrazide, isonicotinic acid hydrazide, etc.

In order to further improve the shelf life of the epoxy resin composition according to the present invention, when the addition reaction is conducted with the above mentioned epoxy compound and amine compound to produce the latent curing accelerator to be used according to the present invention, an active hydrogen compound having 2 or more active hydrogen atoms in its molecule may be added thereto as a third component. Examples of such an active hydrogen compound are given below, but it is not limited thereto.

It may be, for example, a polyhydric phenol such as bisphenol A, bisphenol F, bisphenol S, hydroquinone, catechol, resorcinol, pyrogallol, phenolic novolac resin, etc.; a polyhydric alcohol such as trimethylolpropane, etc.; a polyhydric carboxylic acid such as adipic acid, phthalic acid, etc.; or 1,2-dimercaptoethane, 2-mercaptoethanol, 1-mercapto-3-phenoxy-2-propanol, mercaptoacetic acid, anthranilic acid, lactic acid, etc.

Representative examples are given below of the isocyanate compound to be used as the surface treatment agent for the production of the latent curing accelerator used according to the present invention, but it is not limited thereto these examples.

It may be, for example, a monofunctional isocyanate compound such as n-butyl isocyanate, isopropyl isocyanate, phenyl isocyanate, benzyl isocyanate, etc.; a polyfunctional isocyanate compound such as hexamethylene diisocyanate, toluene diisocyanate, 1,5-naphthalene diisocyanate, diphenylmethane-4,4'-diisocyanate, isophorone diisocyanate, xylylene diisocyanate, p-phenylene diisocyanate, 1,3,6-hexamethylene triisocyanate, bicycloheptane triisocyanate, etc.; and also terminal isocyanate-containing compounds obtained by reactions of these polyfunctional isocyanate compounds and active hydrogen compounds may be used, examples of which include a terminal isocyanate-containing addition reaction product obtained by a reaction of tolylene diisocyanate with trimethylolpropane, and a terminal isocyanate-containing addition reaction product obtained by a reaction of tolylene diisocyanate with pentaerythritol.

The acidic substance to be used as the surface treatment agent for the production of the latent curing accelerator used according to the present invention may be a gaseous or liquid inorganic or organic acid, and representative examples thereof are given below; however, it is not limited to these examples.

It may be, for example, carbon dioxide, sulfur dioxide, sulfuric acid, hydrochloric acid, oxalic acid, phosphoric acid, acetic acid, formic acid, propionic acid, adipic acid, caproic acid, lactic acid, succinic acid, tartaric acid, sebacic acid, p-toluenesulfonic acid, salicylic acid, boric acid, tannic acid, alginic acid, polyacrylic acid, polymethacrylic acid, phenol, pyrogallol, phenol resin, resorcin resin, etc.

The latent curing accelerator to be used according to the present invention may be easily obtained mixing the above mentioned components (a) an epoxy compound and (b) an amine compound, or (a) an epoxy compound, (b) an amine compound and (c) an active hydrogen compound, and reacting them at from room temperature to 200°C, and then solidifying and crushing the product thereof, or by reacting them in a solvent such as methyl ethyl ketone, dioxane, tetrahydrofuran or the like, removing the solvent, and then crushing the solid fraction thereof. Furthermore, the surface treatment of these latent curing accelerators may be carried out by contacting them with any of the above mentioned isocyanate compounds or acidic compounds in a solvent such as methyl ethyl ketone, toluene, etc. or with no solvent.

Commercially available representative examples of the above mentioned solid dispersion-type amine adduct latent curing accelerator are given below, but it is not limited to these examples. For example, mention may be made of "Ajicure PN-23" (trademark, Ajinomoto, Inc.), "Ajicure PN-H" (trademark, Ajinomoto, Inc.), "Ajicure MY-24" (trademark, Ajinomoto, Inc.), "Hardener X-3661S" (trademark, A.C.R. Co., Ltd.), "Hardener X-3670S" (trademark, A.C.R. Inc.), "Novacure HX-3742" (trademark, Asahi Chemical Industry Co., Ltd.), "Novacure HX-3721" (trademark, Asahi Chemical Industry Co., Ltd.), etc.

The compound to be used according to the present invention which is obtained by a reaction between a compound which contains one or more isocyanate groups in its molecule and a compound which has at least one primary and/or secondary amino group in its molecule, may be obtained by reacting the isocyanate with a compound which has a primary and/or secondary amino group in an organic solvent such as dichloromethane.

As the above mentioned compound which contains one or more isocyanate groups in its molecule may be mentioned, for example, n-butyl isocyanate, isopropyl isocyanate, 2-chloroethyl isocyanate, phenyl isocyanate, p-bromophenyl isocyanate, m-chlorophenyl isocyanate, o-chlorophenyl isocyanate, p-chlorophenyl isocyanate, 2,5-dichlorophenyl isocyanate, 3,4-dichlorophenylisocyanate, 2,6-dimethylphenyl isocyanate, o-fluorophenyl isocyanate, p-fluorophenyl isocyanate, m-tolyl isocyanate, p-tolyl isocyanate, o-trifluoromethylphenyl isocyanate, m-trifluoromethylphenyl isocyanate, benzyl isocyanate, hexamethylene diisocyanate, 2,4-tolulene diisocyanate, 2,6-tolulene diisocyanate, 1,5-naphthalene diisocyanate, diphenylmethane-4,4'-diisocyanate, 2,2-dimethyldiphenylmethane-4,4'-diisocyanate, tolidine diisocyanate, isophorone diisocyanate, xylene diisocyanate, 1,3-bis(isocyanate methyl) cyclohexane, p-phenylene diisocyanate, 1,3,6-hexamethylene triisocyanate, bicycloheptane triisocyanate, tris-(3-isocyanato-4-methylphenyl) isocyanurate, tris-(6-isocyanatohexyl) isocyanurate, etc., but the compound is not limited to these examples.

As the compound which has at least one primary and/or secondary amino group in its molecule and which reacts with the isocyanate may be mentioned, for example, dimethylamine, diethylamine, di-n-propylamine, di-n-butylamine, di-n-hexylamine, di-n-octylamine, di-n-ethanolamine, dimethylaminopropylamine, diethylaminopropylamine, morpholine, piperidine, 2,6-dimethylpiperidine, 2,2,6,6-tetramethylpiperidine, piperazine, pyrrolidine, benzylamine, N-methylbenzylamine, cyclohexylamine, m-xylylenediamine, 1,3-bis (aminomethyl) cyclohexane, isophoronediamine, N-aminoethylpiperazine, 2-methylimidazole, 2-ethyl-4-methylimidazole, 2-undecylimidazole, 2-phenylimidazole, 1,1-dimethylhydrazine, etc., but the compound is not limited to these examples.

In addition, as the accelerator may be used a solid dispersion-type latent curing accelerator, such as the one described in Japanese Patent Application Publication HEI 3-296525 which is obtained by reacting an epoxy resin having 2 or more epoxy groups in its molecule as a third ingredient during a reaction with N,N-dialkylaminoalkylamine, an amine having an active hydrogen atom in its molecule and having a cyclic structure which includes one or two nitrogen atoms, and a diisocyanate.

Commercially available dispersion-type latent curing accelerators include "Fujicure FXE-1000" (trademark, Fuji Chemical Industry Co., Ltd.), "Fujicure FXR-1030" (trademark, Fuji Chemical Industry Co., Ltd.), etc.

The mixing ratio of the epoxy resin and polythiol compound in the epoxy resin composition according to the present invention is a ratio of epoxy equivalents (SH equivalents) = 0.5-1.2, and the amount to be added of the solid dispersion-type latent curing accelerator or the compound obtained by a reaction of a compound which contains one or more isocyanate groups in its molecule with a compound which has at least one primary and/or secondary amino group in its molecule, is 0.1-10 parts by weight to 100 parts by weight of the epoxy resin.

According to need, any number of additives may be added to the epoxy resin composition according to the present invention, including fillers, diluting agents, solvents, pigments, flexibilizer, coupling agents, anti-oxidants, and the like.

If an isocyanate group-containing compound is used as an additive, then the adhesive strength may be improved without significantly impairing the curability of the resin. Such an isocyanate-containing compound to be used is not particularly limited, and representative examples thereof include n-butyl isocyanate, isopropyl isocyanate, 2-chloroethyl isocyanate, phenyl isocyanate, p-chlorophenyl isocyanate, benzyl isocyanate, hexamethylene diisocyanate, 2-ethylphenyl isocyanate, 2,6-dimethylphenyl isocyanate, 2,4-toluene diisocyanate, 2,6-toluene diisocyanate, 1,5-naphthalene diisocyanate, diphenylmethane-4,4'-diisocyanate, tolidine diisocyanate, isophorone diisocyanate, xylylene diisocyanate, paraphenylene diisocyanate, 1,3,6-hexamethylene triisocyanate, bicycloheptane triisocyanate, etc.

The amount of the isocyanate group-containing compound to be added to the epoxy resin composition according to the present invention is in the range of 0.1-20 parts by weight to 100 parts by weight of the epoxy resin.

### Examples

A more detailed description of the present invention is provided below with reference to the following Examples.

#### (Method of Evaluation)

**Shelf life:** The prepared epoxy resin composition was poured into a 50 ml glass sampling bottle, and measurement was taken of the time required for the initial viscosity to double when measured at 25°C using a B-type viscosimeter.

Working life: The prepared epoxy resin composition was poured into a 50 ml glass sampling bottle, and measurement was taken of the time required for the flowability to disappear at 25 ° C.

Viscosity: Measurement was made based on JIS K-6833.

Gel time: Measurement was made using a Yasuda gel timer.

5 Tensile shear adhesive strength: A sample prepared based on JIS K-6850 was cured at a specific temperature and for a specific time, and the tensile shear adhesive strength was measured using a Tensilon Universal Testing Machine (Tensilon UTM-5T, product of Toyo Seiki, Inc.).

Measuring temperature: 25 ° C

Tension speed: 1 mm/min

10 T-peel adhesive strength: A sample prepared based on JIS K-6854 was cured at a specific temperature and for a specific time, and the tensile shear adhesive strength was measured using a Tensilon Universal Testing Machine (Tensilon RTM-500, product of Orientech, Inc.).

Measuring temperature: 25 ° C

Tension speed: 50 mm/min

15 Alkali metal ion concentration: Assay was made according to the atomic absorption method, using a flame spectrophotometer (Hitachi Model 180-50).

The names of the materials used in the Examples are as follows.

(1) Epoxy resin

20 "EP-828" (trade name, Yuka Shell Epoxy Co.)

Bisphenol A-type epoxy resin with epoxy equivalents 184-194

"EP-152" (trade name, Yuka Shell Epoxy Co.)

Phenolic novolac-type epoxy resin with epoxy equivalents 172-178

25 "EP-154" (trade name, Yuka Shell Epoxy Co.)

Phenolic novolac-type epoxy resin with epoxy equivalents 176-180

(2) Polythiol compound

30 "TMTP" (trade name, Yodo Kagaku Co.)

Trimethylolpropane tris( $\beta$ -thiopropionate)

$K^+ < 0.5$  ppm,  $Na^+ < 2.9$  ppm

"TMTP" (trade name, Yodo Kagaku Co.)

Trimethylolpropane tris( $\beta$ -thioglycolate)

35 "PETG" (trade name, Yodo Kagaku Co.)

Pentaerythritol tetrakis(thioglycolate)

"PETP" (trade name, Yodo Kagaku Co.)

Pentaerythritol tetrakis( $\beta$ -thiopropionate)

40 Preparation 1

A 100 g portion of the thiol-type curing agent "Epomate QX-12" (trade name, Yuka Shell Co.) was placed in a 1 liter Erlenmeyer flask, and 500 ml of acetone was added thereto for dissolution. The solution exhibited strong alkalinity on pH test paper. Concentrated hydrochloric acid was added dropwise to the solution while stirring to adjust the pH of the solution to weak acidity, and then the solvent was distilled off under reduced pressure. To the residue was added 500 ml of distilled water, and extraction was performed 3 times with 500 ml of chloroform. Anhydrous magnesium sulfate was added to the organic layer and the mixture was allowed to stand overnight, after which the magnesium sulfate was filtered off and the filtrate was concentrated under reduced pressure to obtain purified QX-12. The alkali metal ion concentration of this substance was  $K^+ = 11.2$  ppm and  $Na^+ = 1420$  ppm prior to dealkalization treatment, but fell to  $K^+ = 0.5$  ppm or less and  $Na^+ = 3.2$  ppm after dealkalization treatment.

Preparation 2

55 A 20 g portion of "Epomate QX-12" was placed in a 300 ml Erlenmeyer flask, and 200 ml of methanol was added thereto for dissolution. To this solution was added 20 g of the cation exchange resin "Daia-ion PK216H" (product of Mitsubishi Kasei, Inc.), and the mixture was stirred for 3 hours. The ion exchange resin was then filtered off, and the filtrate was concentrated under reduced pressure to obtain purified QX-12. The

alkali metal ion concentration of this substance was  $K^+ = 2.2$  ppm and  $Na^+ = 7.9$  ppm.

### Preparation 3

5 To a 500 ml three neck flask equipped with a drop funnel were added 50 g of phenyl isocyanate and 200 ml of dichloromethane, and 25 g of 1,1-dimethylhydrazine was added dropwise thereto while stirring on ice. After dropping, the mixture was returned to room temperature and stirred for 3 hours, after which the dichloromethane was distilled off under reduced pressure to obtain a white, solid crude product. The obtained crude product was washed with 200 ml of petroleum ether to obtain 72 g (96% yield) of N-phenyl-N',N'-dimethylaminourea.  
10

### Example 1

To a mixture prepared by adding 1 part by weight of "Ajicure PN-H" to 10 parts by weight of the bisphenol A-type epoxy resin "EP828" (trade name, Yuka Shell Co.) at room temperature was added 90 parts by weight of the purified QX-12 obtained in Preparations 1 and 2, and this was mixed at room temperature to obtain epoxy resin compositions (i) and (ii). The working life for both compositions (i) and (ii) was 3 hours. Also, the gel time for composition (ii) at 60 °C was 925 seconds.  
15

### Comparison 1

Epoxy resin composition (iii) was obtained in the same manner as in Example 1, except that non-dealkalinized "Epomate QX-12" was used as the polythiol compound. The working life for composition (iii) was 3 minutes.  
20

### Examples 2-5

Epoxy resin compositions (iv) - (vii) were prepared using "EP828" as the epoxy resin, "TMTP" (trimethylolpropane tris( $\beta$ -thiopropionate), trade name of Yodo Kagaku Co.  $K^+ < 0.5$  ppm,  $Na^+ : 2.9$  ppm) as the polythiol compound, and the substances shown in Table 1 as the solid dispersion-type amine adduct latent curing accelerators. The properties of compositions (iv) - (vii) are shown in Table 1.  
25

### Comparisons 2-7

Epoxy resin compositions (viii) - (xiii) were prepared in the same manner as in Examples 2-5, except that, instead of the solid dispersion-type amine adduct latent curing accelerators were used the liquid accelerators "Epomate B-02" (adduct of 3,9-bis(aminopropyl)-2,4,8,10-tetraoxaspro-[5,5]-undecane and butylglycidyl ether (liquid), trade name of Yuka Shell Co.), "2E4MZ" (2-ethyl-4-methylimidazole, trade name of Shikoku Kasei) and "DMP-30" (2,4,6-tris(dimethylaminomethyl) phenol). The properties of compositions (viii) - (xiii) are shown in Table 1. The present invention is characterized by providing a long working life and allowing a short curing time in comparison to the examples in which liquid or soluble amine compounds were used as the accelerators.  
35  
40

### Example 6

To 100 parts by weight of "EP828" was added 2 parts by weight of "Ajicure PN-H", and these were mixed at room temperature, after which "TMTP" was added thereto and the components were mixed while defoaming to prepare epoxy resin compositions (xiv) - (xviii). The properties of each of the compositions and their properties after curing at 80 °C for 20 minutes are shown in Table 2.  
45  
50

### Example 7

To 100 parts by weight of "EP828" was added 3 parts by weight of "Ajicure PN-H", and these were mixed at room temperature, and then 74 parts by weight of "TMTP" was added thereto and the components were mixed while defoaming, after which "MR-200" (diphenylmethane-4,4'-diisocyanate: product of Nippon Polyurethane, Inc.) was added thereto, to prepare epoxy resin compositions (xiv) - (xxii). The gel times at 80 °C and the shear adhesive strengths after curing at 80 °C for 20 minutes for each of the compositions are shown in Table 3.  
55



Example 8

In the polythiol compounds listed in Table 4 was dissolved at room temperature 3 parts by weight of the N-phenyl-N',N'-dimethylaminourea obtained in Preparation 3, 100 parts by weight of "EP-828" was added thereto, and the components were mixed while defoaming to obtain epoxy resin compositions (xxiii) - (xxviii). Compositions (xxiii) - (xxviii) were completely uniform liquids. The properties of compositions (xxiii) - (xxviii) are shown in Table 4.

Example 9

In 51 parts by weight of "PETP" was dissolved at room temperature 3 parts by weight of N-phenyl-N',N'-dimethylaminourea, 100 parts by weight of an epoxy resin was added thereto, and the components were mixed while defoaming to obtain epoxy resin compositions (xxix) - (xxx). Compositions (xxix) - (xxx) were completely uniform liquids. The properties of compositions (xxix) - (xxx) are shown in Table 5.

Example 10

In 74 parts by weight of "TMTP" was dissolved at room temperature 3 parts by weight of a urea compound which was produced by a reaction of phenyl isocyanate and diethylamine, 100 parts by weight of "EP-828" was added thereto, and the components were mixed while defoaming to obtain epoxy resin composition (xxxi). Composition (xxxi) was a completely uniform liquid. The gel time of composition (xxxi) at 120 °C was 10 minutes, and its gel time at 100 °C was 24 minutes. The initial viscosity was 13 poise at 25 °C. Also, the shelf life was 10 days.

Example 11

In 74 parts by weight of "TMTP" was dissolved at room temperature 1 part by weight of a urea compound which was produced by a reaction of phenyl isocyanate and diethylamine, 100 parts by weight of "EP-828" was added thereto, and the components were mixed while defoaming to obtain epoxy resin composition (xxxii). Composition (xxxii) was a completely uniform liquid. The gel time of composition (xxxii) at 120 °C was 15 minutes, and its gel time at 100 °C was 36 minutes. The initial viscosity was 10 poise at 25 °C. Also, the shelf life was 2 weeks.

Example 12

In 74 parts by weight of "TMTP" was dissolved at room temperature 3 parts by weight of a urea compound which was produced by a reaction of phenyl isocyanate and di-n-butylamine, 100 parts by weight of "EP-828" was added thereto, and the components were mixed while defoaming to obtain epoxy resin composition (xxxiii). Composition (xxxiii) was a completely uniform liquid. The gel time of composition (xxxiii) at 120 °C was 14 minutes. The initial viscosity was 7 poise at 25 °C. Also, the shelf life was 3 weeks.

Example 13

One hundred parts by weight of "EP-828" and 3 parts by weight of 2,4-bis (N,N-dimethylurea) toluene were kneaded together, 74 parts by weight of "TMTP" was added thereto, and the components were stirred and mixed to obtain epoxy resin composition (xxxiv). Composition (xxxiv) was a completely uniform liquid. The gel time of composition (xxxiv) at 80 °C was 12 minutes. Also, the working life was 5 days.

Example 14

One hundred parts by weight of "EP-828" was mixed and kneaded with 3 parts by weight of the product of a reaction of tris-(3-isocyanato-4-methylphenyl) isocyanurate and 2-methylimidazole, 74 parts by weight of "TMTP" was added thereto, and the components were stirred and mixed to obtain epoxy resin composition (xxxv). The gel time of composition (xxxv) at 80 °C was 20 minutes. Also, the working life was 3 days.



Example 15

One hundred parts by weight of "EP-828" was kneaded with 3 parts by weight of the product of a reaction of tris-(3-isocyanato-4-methylphenyl) isocyanurate and dimethylaminopropylamine, 74 parts by weight of "TMTP" was added thereto, and the components were stirred and mixed to obtain epoxy resin composition (xxxvi). The gel time of composition (xxxvi) at 80 ° C was 12 minutes. Also, the working life was 1 month.

Example 16

To 100 parts by weight of "EP-828" was added 1 part by weight of "Fujicure FXE-1000" and these were mixed at room temperature, after which 74 parts by weight of "TMTP" was added thereto, and the components were mixed while defoaming to obtain epoxy resin composition (xxxvii). The gel time of composition (xxxvii) at 80 ° C was 5 minutes, and the gel time at 60 ° C was 18 minutes. The initial viscosity was 3 poise at 25 ° C. Also, the working life was 5 days.

As mentioned above, a polythiol epoxy resin composition according to the present invention has excellent curability at relatively low heating temperatures and provides strong adhesive strength, and thus is suitable for use in adhesive agents, sealing agents, casting materials and the like. By adding an isocyanate group-containing composition to the epoxy resin composition according to the present invention, the adhesive strength may be improved without significantly impairing the curability of the resin. In addition, an epoxy resin composition according to the present invention has a very long working life, and therefore it is extremely useful from the point of view of improving working efficiency. Furthermore, since it is possible to preserve the excess composition after use, there is no longer any need to discard it, and as a result the composition according to the present invention is extremely useful from the standpoint of conservation of resources and environmental protection, as well.

Table 1

	Epoxy	Epoxy Resine	Thiol Compound	Curing Accelerator	Initial Viscosity (poise)	Gel Time (second)	Working Life
	Composition	/ Parts	/ Parts	/ Parts		60 °C	80 °C
Example 2	iv	EP828 / 100	TNTP / 74	Ajicure PN-H / 1	13.0	1398	314 7 days
Example 3	v	EP828 / 100	TNTP / 74	Ajicure MY-24 / 1	13.0	485	144 8 hrs
Example 4	vi	EP828 / 100	TNTP / 74	Novacure HX-3742/ 3	13.0	1772	380 7 days
Example 5	vii	EP828 / 100	TNTP / 74	Novacure HX-3721/ 1	13.0	2598	666 1 day
Comparison 2	viii	EP828 / 100	TNTP / 74	TDAMP* / 1	13.0	-	275 25 min
Comparison 3	ix	EP828 / 100	TNTP / 60	m-Xylenediamine / 4	15.0	-	>7200 17 hrs
Comparison 4	x	EP828 / 100	TNTP / 60	Ethanolamine / 5	15.0	-	2478 30 min
Comparison 5	xi	EP828 / 100	TNTP / 60	Epomate B-02 / 10	18.0	-	3729 4 hrs
Comparison 6	xii	EP828 / 100	TNTP / 74	2E4M2 / 5	14.0	-	451 8 hrs
Comparison 7	xiii	EP828 / 100	TNTP / 74	DMP-30 / 1	13.0	-	275 25 min

\* TDAMP : Tris(dimethylaminomethyl)phenol

Table 2

Epoxy Composition	xiv	xv	xvi	xvii	xviii
EP828	100	100	100	100	100
TMTP	74	66	59	52	44
Ajicure PN-H	2	2	2	2	2
Gel Time 80°C	213	204	184	175	169
Working Life	3 days	3 days	3 days	4 days	4 days
Tensile Shear Adhesive Strength	210	209	186	145	76
T-peel Adhesive Strength	1.0	1.1	4.8	8.1	8.9
	(Parts)	(Parts)	(Parts)	(Parts)	(Parts)
	(sec)				
	(kgf/cm <sup>2</sup> )				
	(kgf/25mm)				

Table 3

Epoxy Composition		xix	xx	xxi	xxii
EP828	(Parts)	100	100	100	100
TMTF	(Parts)	74	74	74	74
Ajicure PN-H	(Parts)	3	3	3	3
MR-200	(Parts)	0	1	4	10
Gel Time 80 °C	(sec)	109	117	123	130
Tensile Shear Adhesive Strength	(kgf/cm <sup>2</sup> )	210.0	215.7	230.7	255.1



Table 4

Epoxy Composition	xxiii	xxiv	xxv	xxvi	xxvii	xxviii
EP828	(Parts) 100	100	100	100	100	100
TMTP	(Parts) 70	0	0	0	0	0
TMTG	(Parts) 0	63	0	0	0	0
PETG	(Parts) 0	0	57	0	0	0
PETP	(Parts) 0	0	0	64	51	38
N-Phenyl-N',N'-dimethylaminourea	(Parts) 3	3	3	3	3	3
Gel Time 100 °C	(min) -	-	64	46	44	35
Gel Time 120 °C	(min) 23	25	19	18	19	17
Initial Viscosity	(poise) 10	13	37	27	36	46
Shelf Life	(week) 3	3	3	4	4	4
Water Absorption in Boiling Water 1H (%)	0.7	0.8	0.8	0.8	-	-
Tensile Shear Adhesive Strength	(kgf/cm <sup>2</sup> ) -	-	-	-	226	-
T-peel Adhesive Strength	(kgf/25mm) -	-	-	-	3.3	-

Table 5

Epoxy Composition	XXIX		XXX	
EP828	(Parts)	0	50	
EP-152	(Parts)	100	0	
EP-154	(Parts)	0	50	
PETP	(Parts)	51	51	
N-Phenyl-N',N'-dimethylaminourea	(Parts)	3	3	
Gel Time 100 °C	(min)	38	38	
Gel Time 120 °C	(min)	15	14	
Initial Viscosity	(poise)	81	160	
Shelf Life	(week)	3	3	

### Claims

1. An epoxy resin composition comprising (1) an epoxy resin which has 2 or more epoxy groups in its molecule, (2) a polythiol compound which has 2 or more thiol groups in its molecule and (3) a solid dispersion-type amine adduct latent curing accelerator.
2. An epoxy resin composition comprising (1) an epoxy resin which has 2 or more epoxy groups in its molecule, (2) a polythiol compound which has 2 or more thiol groups in its molecule and (3) the product of a reaction between a compound which contains one or more isocyanate groups in its molecule and a compound which has at least one primary and/or secondary amino group in its molecule.
3. An epoxy resin composition according to claim 1, wherein (3) the solid dispersion type amine adduct latent curing accelerator is the product of the reaction between an amine compound and an epoxy compound and optionally a compound having two or more active hydrogen atoms in its molecule, which is insoluble in the epoxy resin at room temperature.
4. An epoxy resin composition according to any of the claims 1 to 3, characterized by being obtained by adding an isocyanate group-containing composition to an epoxy resin composition according to Claim 1, 2 or 3, at a proportion of 0.1-20 parts by weight to 100 parts by weight of the epoxy resin.
5. A cured epoxy resin obtained by heating an epoxy resin composition according to any of the claims 1 to 4.

(19)



Europäisches Patentamt  
European Patent Office  
Office européen des brevets



(11)

Publication number:

**0 594 133 A3**

(12)

**EUROPEAN PATENT APPLICATION**

(21)

Application number: 93116889.2

(51)

Int. Cl.<sup>6</sup>: C08G 59/68, C08G 59/66

(22)

Date of filing: 19.10.93

(30)

Priority: 22.10.92 JP 284300/92  
23.08.93 JP 227851/93  
23.08.93 JP 227852/93

(43)

Date of publication of application:  
27.04.94 Bulletin 94/17

(84)

Designated Contracting States:  
DE FR GB

(86)

Date of deferred publication of the search report:  
04.01.95 Bulletin 95/01

(71)

Applicant: Ajinomoto Co., Inc.  
No. 15-1, Kyobashi 1-chome  
Chuo-ku  
Tokyo (JP)

(72)

Inventor: Sakata, Hiroyuki, c/o Central  
Research Lab.  
Ajinomoto Co., Inc.,  
1-1 Suzuki-cho,  
Kawasaki-ku  
Kawasaki-shi,  
Kanagawa-ken (JP)  
Inventor: Yokota, Tadahiko, c/o Central  
Research Lab.  
Ajinomoto Co., Inc.,  
1-1 Suzuki-cho,  
Kawasaki-ku  
Kawasaki-shi,  
Kanagawa-ken (JP)  
Inventor: Mori, Kenichi, c/o Central Research

Lab.

Ajinomoto Co., Inc.,  
1-1 Suzuki-cho,  
Kawasaki-ku  
Kawasaki-shi,  
Kanagawa-ken (JP)

Inventor: Hirai, Kiyomiki, c/o Central Research  
Lab.

Ajinomoto Co., Inc.,  
1-1 Suzuki-cho,  
Kawasaki-ku  
Kawasaki-shi,  
Kanagawa-ken (JP)

Inventor: Takeuchi, Koji, c/o Central Research  
Lab.

Ajinomoto Co., Inc.,  
1-1 Suzuki-cho,  
Kawasaki-ku  
Kawasaki-shi,  
Kanagawa-ken (JP)

Inventor: Hatajima, Toshihiko, c/o Central  
Research Lab.

Ajinomoto Co., Inc.,  
1-1 Suzuki-cho,  
Kawasaki-ku  
Kawasaki-shi,  
Kanagawa-ken (JP)

(74)

Representative: Strehl Schübel-Hopf Groening  
& Partner  
Maximilianstrasse 54  
D-80538 München (DE)

(54)

Polythiol epoxy resin composition with extended working life.

(57)

An epoxy resin composition which contains (1) an epoxy resin which has 2 or more epoxy groups in its molecule, (2) a polythiol compound which has 2 or more thiol groups in its molecule and (3) a solid dispersion-type amine adduct latent curing accelerator or the product of a reaction between a compound which contains one or more isocyanate groups in its

molecule and a compound which has at least one primary and/or secondary amino group in its molecule.

EP 0 594 133 A3



European Patent  
Office

## EUROPEAN SEARCH REPORT

Application Number  
EP 93 11 6889

DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int.Cl.5)
A	FR-A-1 403 184 (SHELL INTERNATIONALE RESEARCH MAATSCHAPPIJ B.V.) * page 1 - page 4 * ---	1,5	C08G59/68 C08G59/66
A	FR-A-1 080 866 (UNION CARBIDE AND CARBON CORP.) * claims 1,14; examples 4-6 * ---	1,5	
A	DATABASE WPI Week 8732, Derwent Publications Ltd., London, GB; AN 87-224928 & JP-A-62 149 778 (SUMITOMO BAKELITE KK) 3 July 1987 * abstract * ---	1,5	
A	DATABASE WPI Week 8127, Derwent Publications Ltd., London, GB; AN 81-48830D & JP-A-56 057 820 (CEMEDYNE KK) 20 May 1981 * abstract * ---	1,5	
A	US-A-4 562 241 (A. RENNER) * abstract * -----	2	
The present search report has been drawn up for all claims			
Place of search BERLIN		Date of completion of the search 3 November 1994	Examiner Krische, D
<b>CATEGORY OF CITED DOCUMENTS</b> X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons ----- & : member of the same patent family, corresponding document			

EPO FORM 1503 01.83 (P04C01)